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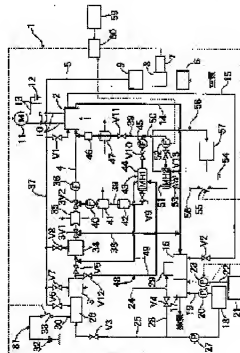
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(54) RECYCLING DEVICE OF HYDROGEN STORAGE ALLOY IN FUEL CELL OPERATING SYSTEM

(57)Abstract:

PROBLEM TO BE SOLVED: To recycle hydrogen storage alloy and aim at prolonging its life.

SOLUTION: In a fuel cell operating system equipped with a reformer 3 forming hydrogen from raw materials such as alcohols, gasolines or the like, a hydrogen reservoir 51 installed by the hydrogen storage alloy MH2 that can occlude and discharge generated hydrogen by the reformer 3, the regenerator of hydrogen storage alloy has a deterioration detecting means 52 which detects that the hydrogen storage alloy MH2 is deteriorated by an adhesion of impurities, a residual amount detecting means 53 which detects that the amount of remaining occluded hydrogen in the hydrogen reservoir 51 reached the amount which is necessary for the regeneration of hydrogen storage alloy, and a heating means 56 that heats the hydrogen storage alloy MH2 in order to remove the impurities by emitted hydrogen based on the both detected signal of the deterioration detecting means 52 and residual amount detecting means 53.



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Notes:

1. Untranslatable words are replaced with asterisks (* **).
2. Texts in the figures are not translated and shown as it is.

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Dictionary: Last updated 06/06/2009 / Priority: 1. Chemistry / 2. Manufacturing/Quality / 3. JIS (Japan Industrial Standards) term

CLAIM + DETAILED DESCRIPTION

[Claim(s)]

[Claim 1] A reformer (3) which generates hydrogen from raw materials, such as an alcohol and gasoline, A hydrogen storage machine (51, 61) provided with a hydrogen storage material (MH2, MH3) which occlusion of the hydrogen generated by the reformer (3) is carried out, and can emit it, In a fuel cell operation system provided with a fuel cell (2) to which hydrogen emitted from the hydrogen storage machine (51, 61) is supplied, A deterioration detecting means (52, 64) which detects that said hydrogen storage material (MH2, MH3) deteriorated by adhesion of an impurity, A residual volume detection means (52, 65) which detects that a residual hydrogen storage capacity of said hydrogen storage machine (51, 61) reached a quantity required for regeneration of said hydrogen storage material (MH2, MH3), Based on both detection signals of said deterioration detecting means (52, 64) and a residual volume detection means (52, 65), with released hydrogen. Hydrogen storage material playback equipment in a fuel cell operation system having a heating method (56, 70) which heats said hydrogen storage material (MH2, MH3) that said impurity should be removed.

[Detailed Description of the Invention]**[0001]**

[Field of the Invention] This invention A fuel cell operation system and the reformer which generates hydrogen from raw materials, such as an alcohol and gasoline, especially, It is related with the hydrogen storage material playback equipment in the fuel cell operation system provided with the hydrogen storage machine provided with the hydrogen storage material which occlusion of the hydrogen generated by the reformer is carried out, and can emit it, and the fuel cell to which the hydrogen emitted from the hydrogen storage machine is supplied.

[0002]

[Description of the Prior Art] If impurities, such as CO, CO₂, and O₂, are contained in the reformed gas generated by the reformer out of hydrogen which is a principal component and the impurity adheres to a hydrogen storage material, the alloy will deteriorate and a hydrogen storage capacity and a rate of hydrogen absorption will fall.

[0003]Using conventionally the hydrogen storage material to which plating treatment, such as Pd and nickel, was performed as a means to avoid this is adopted.

[0004]

[Problem to be solved by the invention]However, in the case of the hydrogen storage material to which plating treatment was performed, although a hydrogen storage capacity is high compared with an unprocessed thing, a hydrogen storage capacity decreases, therefore is temporally insufficient as a deterioration avoiding means by said impurity. When performing plating treatment to a powdered hydrogen storage material, there is also a problem that work becomes very complicated.

[0005]

[Means for solving problem]An object of this invention is to provide said hydrogen storage material playback equipment removes the impurity and it enabled it to reproduce, when a hydrogen storage material deteriorates by adhesion of an impurity.

[0006]The reformer which generates hydrogen from raw materials, such as an alcohol and gasoline, according to this invention in order to attain said purpose, In the fuel cell operation system provided with the hydrogen storage machine provided with the hydrogen storage material which occlusion of the hydrogen generated by the reformer is carried out, and can emit it, and the fuel cell to which the hydrogen emitted from the hydrogen storage machine is supplied, The deterioration detecting means which detects that said hydrogen storage material deteriorated by adhesion of an impurity, The residual volume detection means which detects that the residual hydrogen storage capacity of said hydrogen storage machine reached a quantity required for regeneration of said hydrogen storage material, Based on both the detection signals of said deterioration detecting means and a residual volume detection means, the hydrogen storage material playback equipment in a fuel cell operation system which has a heating method which heats said hydrogen storage material that released hydrogen should remove said impurity is provided.

[0007]Since released hydrogen from a hydrogen storage material, i.e., a hydrogen atom, is high activity when constituted as mentioned above, make CO, CO₂, O₂, etc. which are impurities react to the hyperactive hydrogen atom, make CH₄, H₂O, etc. generate, and by this. An impurity can be removed from a hydrogen storage material and the regeneration can be performed. It is possible by repeating this regeneration and performing it to aim at the prolongation of life of a hydrogen storage material.

[0008]Since a characteristic flow rate change will arise in a device side when carrying out occlusion of the hydrogen, for example to it if a hydrogen storage material deteriorates, As a heating method, further the existing flowmeter which measures the amount of released hydrogen from a hydrogen storage machine for the existing flowmeter which measures the water supply quantum to a hydrogen storage machine as a deterioration detecting means as a residual volume detection means again. [for the hydrogen desorption from a hydrogen storage machine] Since the required existing heating method can be used, respectively, it is possible to constitute a device inexpensive.

[0009]

[Mode for carrying out the invention][Embodiment 1]

I. The fuel cell operation system 1 shown in the fuel cell operation system chart 1 is carried in the electromobile which uses the fuel cell 2 as a power supply.

[0010]In the system 1, the reformer 3 generates the reformed gas which makes hydrogen a principal component from raw materials, such as an alcohol and gasoline, and the supply side is connected to the

reformed gas entrance side of the fuel cell 2 via the supply line 4. In the supply line 5 for air, the super charger 8 and the intercooler 9 which have the air cleaner 6 and the motor 7 in the introduction side are equipped, and the derivation side is connected to the air entrance side of the fuel cell 2. About two fuel cell of the supply line 5 is equipped with the 1st two way type valve V1. A pair of contact buttons of the fuel cell 2 are connected to the vehicles drive motor 11 via a pair of leads 10, and a pair of contact buttons of the auxiliary battery 12 for motor drives are connected to these leads 10 via a pair of leads 13.

[0011]As for the reformed gas outlet side [of the fuel cell 2], and air exit side, it is connected to the burner 16 for evaporators via the exhaust pipe ways 14 and 15, respectively, and about 16 burner of the exhaust pipe way 15 for air is equipped with the 2nd two way type valve V2. One outlet side of the methanol tank 18 is connected to one entrance side of the evaporator 17 via the supply line 19, and the supply line 19 is equipped with the pump 20. The outlet side of the water tank 21 is connected to the entrance side of another side of the evaporator 17 via the supply line 22, and the supply line 22 is equipped with the pump 23. The outlet side of the evaporator 17 is connected to the introduction side of the reformer 3 via the supply line 24 for mixed vapor which consists of methanol and moisture. The outlet side of another side of the methanol tank 18 is connected to the burner 26 for reformer starting via another supply line 25, and the supply line 25 is equipped with the pump 27 and the 3rd two way type valve V3 one by one from the methanol tank 18 side. In the supply line 25, between the pump 27 and the 3rd two way type valve V3 is connected to electric heater KYATARAIZA 29 of the burner 16 for evaporators via another supply line 28, and about 29 electric heater KYATARAIZA of the supply line 28 is equipped with the 4th two way type valve V4. The burner 26 for reformer starting is provided with the heating circuit 31 which has the switch 33 which consists between the glow plug 30, the cell 32, and it and the burner 26.

[0012]The supply line 4 for reformed gas is equipped with 5th two way type valve V5, CO removal machine 34, and 1st three way type valve 3V1, heat exchanger 35, and 2nd three way type valve 3V2 and the 1st flowmeter 36 one by one from the reformer 3 side. In the supply line 5 for air, the supply line 37 branched from the 1st two way type valve V1 about two-fuel cell upstream branches to three more. It is connected to the burner 26 for reformer starting, the reformer 3, and CO removal machine 34, and about 26 burner, about three reformer, and about 34 CO removal machine of the supply line 37 are equipped with the 6th - the 8th two way type valves V6-V8, respectively. Air is used in the burner 26 for combustion and temperature control, and is used in the reformer 3 for temperature control, and further, with CO removal machine 34, it is used in order to oxidize CO contained in reformed gas to CO₂. 1st three way type valve 3V1 which consists in the outlet side of CO removal machine 34 is connected to the exhaust pipe way 14 for reformed gas of the fuel cell 2 via the 1st by-path pipe way 38.

[0013]In the supply route 4 for reformed gas, between 2nd three way type valve 3V2 which consists in the downstream of the heat exchanger 35, and the entrance the 1st flowmeter 36 and the fuel cell 2 side are connected by the 2nd by-path pipe way 39. The 2nd by-path pipe way 39 is equipped with the 1st stores dept. 44 of the 2nd flowmeter 40, the heat exchanger 41, the water removal machine 42, the 9th two way type valve V9, and the hydrogen storage machine 43, the 10th two way type valve V10, the 3rd flowmeter 45, the 11th two way type valve V11, and the flow control valve 46 one by one from 2nd three way type valve 3V2 side. Between the flow control valve 46 and the 11th two way type valve V11, the heat exchanger 47 is equipped if needed for the improvement in temperature control precision.

[0014]The heating apparatus 48 is attached to the 1st stores dept. 44. The heating apparatus 48 has the

pipeline 49 for reformed gas circulation, the entrance side of the pipeline 49 is connected in the supply line 4 for reformed gas between the reformer 3 and the 5th two way type valve V5, and the outlet side is connected between the 5th two way type valve V5 and CO removal machine 34. The entrance side of the pipeline 49 is equipped with the 12th two way type valve V12.

[0015]. [in the 1st stores dept. 44 downstream of the 2nd by-path pipe way 38] [between the 3rd flowmeter 45 and the 11th two way type valve V11] [via the supply and exhaust pipe way 50 for hydrogen] The 2nd stores dept. 51 of the hydrogen storage machine 43 is connected, and the supply and exhaust pipe way 50 is equipped with the 13th two way type valve V13 and the 4th flowmeter 52 one by one from the 2nd stores dept. 51 side.

[0016]The heating circuit 56 which has the heater 53, the battery 54, and the switch 55, and the cooling circuit 58 which has the cooling unit 57 provided with a radiator, a water pump, a water tank, etc. are attached to the 2nd stores dept. 51.

[0017]. [the switch 55 grade of the heating circuit 56 which has the switch 33, each pumps 20, 23, and 27, and the heater 53 of the heating circuit 31 which has the fuel cell 2, the vehicles drive motor 11, and the glow plug 30] [by making the starting switch 59 into an ON state] Operation control is carried out via ECU60 and, on the other hand, it becomes non-operative by changing the starting switch 59 into an OFF state.

[0018]In the hydrogen storage machine 43, it is possible to carry out occlusion of the hydrogen generated by the reformer 3, and to emit it. The 1st stores dept. 44 has what is called a through type tank with an entrance and an exit, the entrance is connected to the upstream of the 2nd by-path pipe way 39, and an exit is connected to the downstream of the 2nd by-path pipe way 39, respectively, and it fills up with 1st hydrogen storage material MH1 in a tank. The 2nd stores dept. 51 has the usual tank which has an entrance and exit, and it fills up with 2nd hydrogen storage material MH2 in the tank. As shown in drawing 2, it has the characteristics that 1st hydrogen storage material MH1 is low-pressure occlusion and a high temperature discharge type, carries out occlusion of the hydrogen by 80 ** and 0.15MPa, and on the other hand emits hydrogen by 130 ** and 0.8MPa. As such a hydrogen storage material, a $\text{LaNi}_{3.96}\text{Co}_{0.6}\text{aluminum}_{0.44}$ alloy is used. 2nd hydrogen storage material MH2 are high-pressure occlusion and a low-temperature discharge type, carry out occlusion of the hydrogen by 60 ** and 0.5MPa, and, on the other hand, have the characteristics of emitting hydrogen by 30 ** and 0.15MPa. As such a hydrogen storage material, a $\text{MmNi}_{4.04}\text{Co}_{0.6}\text{Mn}_{0.31}\text{aluminum}_{0.05}$ alloy (Mm is a misch metal) is used.

[0019]If constituted as mentioned above, when moving hydrogen to the 2nd stores dept. 51 from the 1st stores dept. 44, hydrogen of high desorption pressure is introduced into the 2nd stores dept. 51 under high temperature from the 1st stores dept. 44 using the hydrogen desorption characteristics of 1st hydrogen storage material MH1, Occlusion of the hydrogen can quickly and fully be compulsorily carried out to 2nd hydrogen storage material MH2. On the other hand, discharge of hydrogen from the 2nd stores dept. 51 is performed at a low temperature.

[0020]II. When impurities, such as CO in reformed gas, CO_2 , and O_2 , adhere to 1st hydrogen storage material MH1 of the 1st stores dept. 44 of a hydrogen storage material playback equipment A. deterioration detecting means, [the impurity] When 1st hydrogen storage material MH1 is heated by 130 ** for every hydrogen desorption, are removed from alloy MH1, but. The temperature at the time of the hydrogen

desorption of 2nd hydrogen storage material MH2 of the 2nd stores dept. 51 is 30 **, under this low temperature, it is difficult to remove the impurity adhering to that alloy MH2, therefore deterioration of 2nd hydrogen storage material MH2 arises.

[0021]Deterioration of such a hydrogen storage material is detected as a characteristic flow rate change, when carrying out occlusion of the hydrogen to it. That is, as it said that a peak arises to a flow rate since the 2nd stores dept. 51 is low pressure in early stages when high-pressure hydrogen is supplied to the 2nd stores dept. 51 from the 1st stores dept. 44 as shown in drawing 3 and hydrogen flows there rapidly, and the flow rate once fell and subsequently rose again after that, it changes. 2nd hydrogen storage material MH2 has not deteriorated, or the grade of deterioration is low, that is, if normal, drawing 3 and the degree of the depression after passing over a peak like indication in solid line are low, but if the grade of deterioration becomes high, that is, it deteriorates so that regeneration is required, the degree of said depression will become high. Then, when the flow rate a at the time of depression decreases 20% from the flow rate b at the time of the depression in the case of being normal that is, the time of being set to $a=0.8b$ is judged to be deterioration. Being able to detect [therefore] this with the 4th flowmeter 52 that measures the amount of hydrogen supplies to the 2nd stores dept. 51, the 4th flowmeter 52 functions considering 2nd hydrogen storage material MH2 having deteriorated by adhesion of an impurity as a deterioration detecting means to detect.

[0022]B. It is heated and regeneration of 2nd hydrogen storage material MH of residual volume detection means 2 is performed by holding for 10 minutes and making hydrogen emit under the temperature of 120 **. In this case, regeneration of 2nd hydrogen storage material MH2 of said quality of the material requires minimum about 0.015 wt(s)% of a hydrogen storage capacity. On the other hand, at the time of hydrogen desorption, the internal pressure of the 2nd stores dept. 51 is regulated by 1 or less MPa from the high pressure gas security rule. Supposing the total of the opening in the 2nd stores dept. 51 and the opening in the pipeline from it to the 13th two way type valve V13 is 3L (liter), in 120 **, as for the amount of released hydrogen for satisfying this, 0.037wt% of a hydrogen storage capacity will serve as upper limit.

[0023]Here, if the hydrogen storage capacity of the full state of the 2nd hydrogen storage part 51 is made into 0.8wt%, hydrogen quantity required for regeneration will be 1.9% ($0.8 \times 0.015 \times 100$) - 4.6% ($0.8 \times 0.037 \times 100$).

[0024]Even if it heats 2nd hydrogen storage material MH2 at 120 **, no occlusion hydrogen can be emitted, but about 5% of the hydrogen storage capacity of full state remains.

[0025]If these are taken into consideration, as shown in the PCT curve at 120 ** of 2nd hydrogen storage material MH2 of drawing 4, The regeneration can fully be performed, keeping the internal pressure of the 2nd stores dept. 51 at 1 or less MPa, if it regenerates, when the residual hydrogen storage capacity of the alloy MH2 turns into 9.6% of below the hydrogen storage capacity (4.6% of +5%) (i.e., below default value) of full state.

[0026]With the 4th flowmeter 52 that measures the amount of hydrogen supplies to the 2nd stores dept. 51, and the amount of hydrogen desorption from the 2nd stores dept. 51. [measurement of such a residual hydrogen storage capacity] Being able to carry [therefore] out, the 4th flowmeter 52 functions as a residual volume detection means which detects that a residual hydrogen storage capacity of the 2nd stores dept. 51 reached a quantity required for regeneration of 2nd hydrogen storage material MH2.

[0027]C. As a heating method of *****, the heating circuit 56 attached to the 2nd stores dept. 51 is made

to serve a double purpose.

[0028]D. A deterioration detection signal and a residue detection signal by the 3rd flowmeter 52 are sent to ECU60, and the switch 55 of the heating circuit 56 opens and closes them under control of ECU60 based on these both detection signals.

[0029]Next, various modes are explained with reference to drawing 1 and drawing 5 - drawing 8.

[0030]A. starting Mohd -- in before this mode start, the hydrogen storage capacity in the 2nd stores dept. 51 of the hydrogen storage machine 43 is in full state. the 1st - the 13th two way type valves V1-V13, and the flow control valve 46 -- "-- it being in a closed" state, and so that reformed gas can be supplied to the burner 16 for evaporators, [1st three way type valve 3V1] That is, it is switched to the 1st stores dept. 44 side, respectively so that it may be switched to the burner 16 side and 2nd three way type valve 3V2 can supply reformed gas to the 1st stores dept. 44 on the other hand that is.,

[0031]In drawing 1 and drawing 3, when the starting switch 59 is made into an ON state, the super charger 8 operates and, in air, the 1st two way type valve V1 through the air cleaner 6, the super charger 8, and the intercooler 9, [""""] The fuel cell 2 is supplied and the 6th - the 8th two way type valves V6-V8 are supplied to the burner 26, the reformer 3, and CO removal machine 34 of the reformer 3 by """"", respectively. The 2nd two way type valve V2 is """"", and the air discharged from the fuel cell 2 is introduced into the burner 16 for evaporators.

[0032]If electric heater KYATARAIZA 29 of the burner 16 for evaporators energizes and it carries out temperature up, the pump 27 operates, and methanol will be injected by electric heater KYATARAIZA 29 by """"", the 4th two way type valve V4 will burn the methanol with the burner 16, and heating of the evaporator 17 will be performed.

[0033]The switch 55 of the heating circuit 56 of the 2nd stores dept. 51 closes, and the 2nd stores dept. 51 is heated with the heater 53. In this case, temperature up of the 2nd stores dept. 51, therefore 2nd hydrogen storage material MH2 can be carried out in a short time to about 30 ** which is hydrogen desorption temperature. And if the pressure of the entrance and exit portion of the 2nd stores dept. 51 is detected and the pressure amounts to about 0.15 MPa, by """"", occlusion hydrogen of the 2nd stores dept. 51 will be emitted, the 13th and 11th two way type valve V13, V11, and the flow control valve 46 will be supplied to the fuel cell 2, and it will start operation. The amount of hydrogen supplies from the 2nd stores dept. 51 is detected by the 3rd flowmeter 52. Surplus hydrogen in the fuel cell 2 is introduced into the burner 16 for evaporators, burns there, and is used for heating of the evaporator 17.

[0034]In the burner 26 for reformer starting, the switch 33 of the heating circuit 31 which has the glow plug 30 closes, and the glow plug 30 energizes. Methanol is injected for the 3rd two way type valve V3 by the burner 26 by """"", and the reformer 3 is heated by combustion of the methanol. The gas temperature of the feed hopper portion of the reformer 3 is detected, the switch 33 opens the time of it reaching a predetermined value as the completion of heating of the reformer 3, and the energization to the glow plug 30 is stopped.

[0035]The mixed vapor which methanol and water are injected by the evaporator 17 and consists of methanol and moisture is generated, the mixed vapor is supplied to the reformer 3, and reforming is performed.

[0036]Since reformed gas contains remarkable CO, the 5th two way type valve V5 is """"", is introduced into CO removal machine 34, ranks second and 1st three way type valve 3V1 is switched to the burner 16 side, it

is introduced into the burner 16 through the 1st by-path pipe way 38, and inflammable components, such as hydrogen, burn there.

[0037]When the CO concentration of reformed gas is detected, or CO concentration is investigated from the relation between reformed gas temperature and time and the CO concentration becomes below a predetermined value, 1st and 2nd three way type valve 3V1 and 3V2 are switched to the fuel cell 2 side, and reformed gas is supplied to the fuel cell 2.

[0038]Although the amount of reformed gas from the reformer 3 under warming up is not enough to operate the fuel cell 2, the insufficiency is compensated by released hydrogen of the 2nd stores dept. 51, and, thereby, stabilization of the output of the fuel cell 2 is attained. Reduction control of the amount of hydrogen supplies is gradually carried out with the increase in the amount of reformed gas.

[0039]When the temperature and the pressure of reformed gas in the supply port part of the reformer 3 amount to 200 °C and about 0.16 MPa, respectively, It is judged that the reformer 3 reached stationary mode, and the switch 55 of the heating circuit 56 opens, and the 13th and 11th two way type valve V13 by the side of the 2nd stores dept. 51, V11, and the flow control valve 46 are closed, and it shifts to the autonomous-operation-of-power-system mode by the reformer 3 henceforth.

[0040]When reformed gas passes through the heat exchanger 35 which circulated 50 °C cooling water, the temperature descends at about 80 °C, and the pressure is descending to about 0.15 MPa, respectively, and the reformed gas which has such a temperature and a pressure is used as a fuel in the fuel cell 2.

[0041]B. As shown in hydrogen absorption mode drawing 1 under regular run, and drawing 6, 2nd three way type valve 3V2 is switched to the 1st stores dept. 44 side with the start in hydrogen absorption mode.

[0042]Although the temperature of the reformed gas in 2nd three way type valve 3V2 is about 80 °C and a pressure is about 0.15 MPa, temperature is lowered to the reformed gas by about 60 °C with the heat exchanger 41 which circulated 50 °C cooling water, and, subsequently the water removal machine 42 removes moisture.

[0043]60 °C and the reformed gas of about 0.15 MPa are introduced into the 1st stores dept. 44 for the 9th two way type valve V9 by "****", and occlusion of the hydrogen is carried out to 1st hydrogen storage material MH1. Temperature up of that alloy MH1 is carried out to about 80 °C by this occlusion, and this temperature is held by the cooling action of about 60 °C reformed gas.

[0044]The 10th and 11th two way type valve V10, V11, and the flow control valve 46 are "****", the fuel cell 2 is supplied and, as for reformed gas which passed the 1st stores dept. 44, the operation is continued.

[0045]A hydrogen storage capacity of the 1st stores dept. 44 is detected by difference of ON of the 1st stores dept. 44, and an addition flow rate of the 2nd and 3rd flowmeter 40 and 45 in an outlet side. When a hydrogen storage capacity of the 1st stores dept. 44 has not reached full state, said occlusion process is continued.

[0046]If a hydrogen storage capacity of the 1st stores dept. 44 reaches full state, it will move to a hydrogen shift and the 2nd hydrogen storage material deterioration detection mode.

[0047]C. As shown in a hydrogen shift and 2nd hydrogen storage material deterioration detection mode drawing 1 under regular run, and 7, 2nd three way type valve 3V2 is switched to the fuel cell 2 side.

[0048]the 9th, 10th, and 11th two way type valve V9, V10, and V11 -- "[closed" and the 12th two way type valve V12] ["****] and the 5th two way type valve V5 -- "-- in closed", after about 200 °C high temperature reformed gas circulates the heating apparatus 48, pass CO removal machine 34 and heat exchanger 35

grade -- the fuel cell 2 is supplied and the operation is continued.

[0049]Thus, if 1st hydrogen storage material MH1 of the 1st stores dept. 44 is heated by the exhaust heat of the reformer 3, the temperature rises at about 130 °C and a pressure rises to about 0.8 MPa, occlusion hydrogen will be emitted for the 10th and 13th two way type valve V10 and V13 by "A".

[0050]2nd hydrogen storage material MH2 of the 2nd stores dept. 51 is heated by about 60 °C by the heating circuit 56, and occlusion of the released hydrogen from the 1st stores dept. 44 is carried out to 2nd hydrogen storage material MH2 by 60 °C and about 0.5 MPa. The rise in heat of alloy MH2 by this occlusion is controlled by the cooling circuit 58, and that temperature is held at about 60 °C.

[0051]The flow rate of the hydrogen which flows into the 2nd stores dept. 51 with the 4th flowmeter 52 is measured, and it is detected whether 2nd hydrogen storage material MH2 has deteriorated based on the basis of drawing 3. When having deteriorated, the flag of the purport that regeneration is performed is set after the following starting mode under control of ECU60 based on the detection signal from the 4th flowmeter 52. The Reason for regenerating after starting mode is that occlusion hydrogen of 2nd hydrogen storage material MH2 is emitted for starting, and the residual hydrogen storage capacity is decreasing to near [said] the default value.

[0052]when it is detected by the 3rd flowmeter 45 that is in the outlet side of the 1st stores dept. 44 after said detection that the amount of hydrogen desorption of the 1st stores dept. 44 exceeded 70 percent of the quantity of full state, the 5th two way type valve V5 is "A" -- and the 12th two way type valve V12 -- "-- heating of the 1st stores dept. 44 is suspended by closed." From the 1st stores dept. 44, discharge of hydrogen is continued by the endothermic reaction of 1st hydrogen storage material MH1 using the remaining heat. The temperature of the 1st stores dept. 44 can be lowered by this, and the time lag at the time of resuming the following hydrogen absorption mode can be decreased.

[0053]the time of the addition flow rate of the 3rd flowmeter 45 in the outlet side of the 1st stores dept. 44 reaching the quantity of the full state of the stores dept. 44 -- the 13th two way type valve V13 -- "-- the hydrogen shift to the 2nd stores dept. 51 is suspended by closed." Let the hydrogen storage capacity in the 2nd stores dept. 51 be full state at this time.

[0054]D. As shown in regeneration mode drawing 1 of the 2nd hydrogen storage material, and 8, when it is distinguished after the autonomous-operation-of-power-system mode start by the reformer 3 whether they are whether the deterioration flag of 2nd hydrogen storage material MH2 stands and no and it does not stand, shift to the end of regeneration mode.

[0055]On the other hand, when the deterioration flag stands, the 13th and 11th two way type valve V13, V11, and the flow control valve 46 are "A", and hydrogen is emitted to the fuel cell 2 from the 2nd stores dept. 51 that still holds heat.

[0056]If said hydrogen desorption is continued and it becomes below default value on the other hand when it is detected whether the residual hydrogen storage capacity of 2nd hydrogen storage material MH2 is below said default value and it is over default value with the 4th flowmeter 52, the bottom of control of ECU60 based on the detection signal from the 4th flowmeter 52 -- the 13th two way type valve V13 -- "-- it is closed", and the switch 55 of the heating circuit 56 is closed, 2nd hydrogen storage material MH2 of the 2nd stores dept. 51 is heated with the heater 53, and it is held for 10 minutes under the temperature which is 120 °C. Regeneration is performed in the meantime.

[0057]The switch 55 of the heating circuit 56 is opened, heating of 2nd hydrogen storage material MH2 is

suspended, and regeneration mode results in a stop.

[0058]At the time of this end of regeneration mode, the methane by which occlusion of the gas hydrogen which exists in the 2nd stores dept. 51 was carried out to it with cooling of 2nd hydrogen storage material MH2, and it was generated passes the fuel cell 2 at the time of the next starting, is introduced into the burner 16, and is collected as thermal energy.

[0059][Embodiment 2] Although the fuel cell operation system 1 shown in drawing 9 is carried in an electromobile like Embodiment 1, there is a different point from Embodiment 1 in having stored the hydrogen produced by regeneration. Only required component part is shown in drawing 9 simple on explanation.

[0060]The hydrogen storage machine 61 is the target of regeneration, and the entrance side is connected to the supply side of the reformer 3 via the supply line 62, and the outlet side of the hydrogen storage machine 61 is connected to the hydrogen entrance side of the fuel cell 2 via the supply line 63. The supply line 62 by the side of the reformer 3 is equipped with the 1st flowmeter 64 and the 1st two way type valve V1 as a deterioration detecting means one by one from the reformer 3 side. The supply line 63 by the side of the fuel cell 2 is equipped with the 2nd flowmeter 65 and the 3rd two way type valve V3 as the 2nd two way type valve V2 and a residual volume detection means one by one from the hydrogen storage machine 61 side.

The reserve hydrogen storage machine 66 stores the hydrogen produced by regeneration, and the ON and an outlet side pass the introductory and exhaust pipe way 67 which has the 4th two way type valve V4, and it is connected to the supply line 63 between the 2nd flowmeter 65 and the 3rd two way type valve V3.

[0061]The cooling circuits 74 and 75 provided with the cooling unit 72 which the heating circuits 70 and 71 which equipped the hydrogen storage machine 61 and the reserve hydrogen storage machine 66 with the heating unit 68 which has a battery, a switch, etc., and the heater 69 are attached, and has a water pump, a water tank, a radiator, etc., and the cooling channel 73 are attached. In both the cooling circuits 74 and 75, the cooling unit 72 and the return irrigation canal 76 to that are shared.

[0062]4th hydrogen storage material MH4 which the hydrogen storage machine 61 is filled up with 3rd hydrogen storage material MH3 shown in drawing 10, i.e., a $\text{MmNi}_{4.02}\text{Co}_{0.4}\text{Mn}_{0.28}\text{aluminum}_{0.3}$ (Mm: misch metal) alloy, and is shown in the reserve hydrogen storage machine 66 at drawing 10 -- that is, It fills up with a $\text{MmNi}_{4.12}\text{Co}_{0.6}\text{Mn}_{0.23}\text{aluminum}_{0.05}$ (Mm: misch metal) alloy.

[0063]3rd hydrogen storage material MH3 is held for 10 minutes under temperature of 120 °C in regeneration at said the appearance. A PCT curve of 3rd hydrogen storage material MH3 at these 120 °C is as being shown in drawing 11. On the other hand, in 4th hydrogen storage material MH4, occlusion of the hydrogen emitted by regeneration is carried out in 40 °C and 1MPa. A PCT curve of 4th hydrogen storage material MH4 at these 40 °C is as drawing 12.

[0064]Therefore, the default value of the residual hydrogen content of 3rd hydrogen storage material MH3 at the time of regeneration is set as the value which does not exceed the maximum hydrogen storage capacity in 40 °C of 4th hydrogen storage material MH4, and 1MPa.

[0065]10 kg of powder of 3rd hydrogen storage material MH3 whose a maximum hydrogen storage capacity is 1.2wt% was filled up with this embodiment into the hydrogen storage machine 61, and, on the other hand, 2 kg of powder of 4th hydrogen storage material MH4 whose maximum hydrogen storage capacity at 40 °C is 1.2wt% was filled up with it into the reserve hydrogen storage machine 66. The mean particle diameter of both powder was 15 micrometers, respectively. In this case, said default value which can reproduce 3rd hydrogen storage material MH3 becomes less than 0.24wt%. This is equivalent to 16.7% of the maximum

hydrogen storage capacity of 3rd hydrogen storage material MH3.

[0066]Next, two sorts of Mohd are explained with reference to drawing 9 and drawing 13, and drawing 14.

[0067]A. In starting and driving-modes drawing 9, and drawing 13, starting preparations of making a starting switch into an ON state are made.

[0068]It is distinguished whether they are whether the reserve hydrogen storage machine 66 is empty and no. The reserve hydrogen storage machine 66 is held during a run at a nil state that occlusion of the released hydrogen from the hydrogen storage machine 61 should be carried out at the time of regeneration. the case where it is not empty -- the 1st and 2nd two way type valve V1 and V2 -- "-- it being closed" and in "****", [the 3rd and 4th two way type valve V3 and V4] 4th hydrogen storage material MH4 of the reserve hydrogen storage machine 66 is heated by the heating circuit 71, hydrogen is emitted, the hydrogen is supplied to the fuel cell 2, it is used as a fuel, and, thereby, the fuel cell 2 starts operation.

[0069]on the other hand, when the reserve hydrogen storage machine 66 is empty, the 2nd and 3rd two way type valve V2 and V3 are "****" -- the 4th two way type valve V4 -- "-- in closed", the hydrogen storage machine 61 is heated by the heating circuit 70, hydrogen is supplied to the fuel cell 2, and, thereby, the fuel cell 2 starts operation.

[0070]A run will be started if operation of the fuel cell 2 will be in a stationary state. The amount of released hydrogen from the hydrogen storage machine 61 is measured by the 2nd flowmeter 65.

[0071]B. in re-restoration and 3rd hydrogen storage material regeneration mode drawing 9, and drawing 14 - the 1st two way type valve V1 -- "****", the 2nd - the 4th two way type valves V2-V4 -- "-- in closed", the hydrogen restoration preparations to the hydrogen storage machine 61 from the reformer 3 are made.

[0072]It is distinguished whether they are whether the deterioration flag of 3rd hydrogen storage material MH3 stands and no. When the deterioration flag does not stand, restoration of hydrogen to the hydrogen storage machine 61 is started.

[0073]On the other hand, when the deterioration flag stands, said below default value and no are detected for the residual hydrogen storage capacity of the hydrogen storage machine 61 by the 2nd flowmeter 65, when it is over default value, restoration of hydrogen to the hydrogen storage machine 61 is started, and regeneration of 3rd hydrogen storage material MH3 is turned next time.

[0074]When the residual hydrogen storage capacity of the hydrogen storage machine 61 is below default value, the 1st, 3rd, and 4th two way type valve V1, V3, and V4 -- "-- by closed", in "****", the 2nd two way type valve V2 cools 4th hydrogen storage material MH4 of the reserve hydrogen storage machine 66 at 40 ** by the cooling circuit 75, and, subsequently to "****", carries out the 4th two way type valve V4.

[0075]3rd hydrogen storage material MH3 of the hydrogen storage machine 61 is heated by the heating circuit 70, and it is held for 10 minutes under the temperature of 120 **, and regeneration is performed in the meantime and occlusion of released hydrogen by 4th hydrogen storage material MH4 of the reserve hydrogen storage machine 66 is performed.

[0076]Heating of 3rd hydrogen storage material MH3 by the heating circuit 70 is suspended, and cooling of 4th hydrogen storage material MH4 by the cooling circuit 75 is stopped, and regeneration mode results in a stop.

[0077]the 1st - the 4th two way type valves V1-V4 -- "-- in closed", 3rd hydrogen storage material MH3 of the hydrogen storage machine 61 is cooled by 20 ** by the cooling circuit 74, and, subsequently restoration of hydrogen is performed for the 1st two way type valve V1 by "****".

[0078]The flow rate of the hydrogen which flows into the hydrogen storage machine 61 with the 1st flowmeter 64 is measured, and it is detected whether 3rd hydrogen storage material MH3 has deteriorated based on the basis of drawing 3. When having deteriorated, based on the detection signal from the 1st flowmeter 64, the flag of the purport that regeneration is performed at the time of the next hydrogen restoration is set.

[0079]After the internal pressure (or the amount of hydrogen inflows) of the hydrogen storage machine 61 reaches a predetermined value, the 1st two way type valve V1 is closed, and restoration is ended.

[0080]Drawing 15 shows the relation of the hydrogen absorption and a discharge number of repetitions under 20ppmCO mixing, and hydrogen storage capacity about Example 1 - Example 3.

[0081]Example 1 is related with 3rd hydrogen storage material MH3, it is considered as hydrogen absorption at 20 **, and it makes hydrogen desorption 1 time at 60 **, and when 120 ** and regeneration for 10 minutes are performed like the account of back to front [which performed this 3 times], it corresponds.

[0082]Example 2 is related with 3rd hydrogen storage material MH3, and although hydrogen absorption temperature and hydrogen desorption temperature are the same as Example 1, when it does not regenerate, it corresponds.

[0083]Example 3 is related with the alloy which provided 2.0wt% of Pd plating in 3rd hydrogen storage material MH3, and although hydrogen absorption temperature and hydrogen desorption temperature are the same as Example 1, when it does not regenerate, it corresponds.

[0084]The survival advantage by regenerating, if Example 1 is compared with Example 2 is clear from drawing 15. Although Example 3 is excellent in hydrogen absorption characteristics compared with Example 2, it is distinct that endurance falls temporally compared with Example 1 which regenerates.

[0085]

[Effect of the Invention]According to this invention, the hydrogen storage material playback equipment in a fuel cell operation system possible [aiming at the prolongation of life of a hydrogen storage material] and inexpensive can be provided by constituting as mentioned above.

[Translation done.]